

APPLICATIONS OF LOW TEMPERATURE CO-OXIDATION CATALYSTS
TO BREATHABLE GASES

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SUMMARY

Modifications of tin oxide/precious metal catalysts described for use in CO₂ lasers have also been developed by UOP for use in other applications; namely, as low temperature CO oxidation components in fire escape hoods/masks for mines, aircrafts, hotels, and offices and in sealed environments, such as hyperbaric chambers and submarines. Tin oxide/precious metal catalysts have been prepared on a variety of high surface area cloth substrates for application in fire escape hoods. These show high and stable CO oxidation capability (10^4 ppm CO reduced to 10^1 ppm CO) at GHSV of $37,000 \text{ h}^{-1}$ with water saturated inlet gas at body heat (37°C) and below.

Water vapour plays an important role in the surface state/performance of tin oxide catalyst. Water-resistant formulations have been produced by the introduction of transition metal promoters.

Tin oxide/precious metal catalysts have also been developed for CO oxidation in the North Sea diving environment. These are currently in use in a variety of hyperbaric chambers and diving vehicles. Ambient temperature operation and resistance to atmospheric water vapour have been demonstrated, and as a result, they offer a viable alternative to hopcalite or heated catalyst systems.

A new range of non-tin oxide based low temperature CO oxidation catalysts is described. They are based on reducible metal oxides promoted with precious metals. Preliminary data on selected materials in the form of both cloth artefacts and shaped pellets are presented. They are expected to be applicable both to the breathable gas application area and to CO₂ lasers.

INTRODUCTION

The study of the heterogeneous oxidation of CO has been fruitfully researched by many investigators in heterogeneous catalysis and is still ongoing, as is evident at this workshop. Active catalysts have been prepared from simple oxides and

multicomponent oxides, largely from transition metals, groups III and IV of the periodic table. Many of these oxides contain small amounts of precious metals in order to achieve low temperature catalytic oxidation. Several catalysts have thus far been commercially developed, and although these are of considerable theoretical and practical significance, they do not all possess sufficient activity to warrant their use in, for example gas masks for effective removal of CO from air. For this purpose only the most powerful, highly reactive, oxidising catalysts can be utilized.

Catalysts used in breathable gas systems must initiate the oxidation of CO without an appreciable induction period. The reaction must proceed at the high space velocity required for breathing purposes and under all environmental conditions likely to be encountered in use. The catalyst must have a sufficiently long life and in static systems preferably be regenerable. The catalyst artefact must be sufficiently porous to offer very little resistance to air flow, i.e., low pressure drop across the catalyst bed, and have sufficient chemical stability to withstand prolonged storage at temperature up to 60°C. The ideal catalyst would be one that would be capable of reacting completely with CO in low as well as high gas/air concentration within the temperature range of 0-40°C and not be poisoned by water vapour or small amounts of impurity likely to be encountered in contaminated air.

APPLICATIONS

A major use of low temperature CO oxidation catalyst is in respiratory protection. The latter is necessary where the prevailing breathable environment is not capable of supporting life because of contamination with CO. The most usual circumstances are those involving fires and toxic gases encountered both by the public and fire rescue services. Low temperature CO oxidation catalysts reported here have been developed for this specific purpose, where CO removal down to ppm level is required for air purification and where the catalyst is

1. In granular form and is fitted as part of a life-support system either with or without supplemental oxygen.
2. Deposited on high surface area cloth and incorporated in a smokehood filter device.

These commercial low temperature tin oxide catalysts have found actual and potential use in

1. Diving industry
2. Underground shelters as static systems
3. Smokehoods or portable self-rescue breathing sets
4. Process applications

Diving Industry

Oil explorations in offshore locations have given rise to the need and development of extended duration diving techniques. Using a helium/oxygen mixture as the breathable gas, divers can work for several weeks at depths of up to 300 m. During this time the breathing gas is scrubbed clean of contaminants, such as CO_2 , CO and NO_x , that are produced during respiration and welding operations. Removal of these toxic compounds together with close monitoring of the oxygen levels ensures a high level of diver safety. Precious metals on tin oxide with trace quantities of a promoter provide the CO scrubbing capability.

Typically hydrocarbon and sulphur compounds are removed by appropriate adsorbents upstream of the CO oxidation catalyst.

Underground Shelters

The provision by civil authorities of the safe shelters for the majority of the population in the event of a catastrophe or war is becoming a more acceptable practice. A major consideration in the design of such structures is environmental control equipment to prevent the buildup of toxic gases such as CO produced from smoking and fires and CO_2 from respiration. The precious metals on tin oxide are an appropriate catalyst for this application; it has high tolerance to water vapour and is regenerable.

Smokehoods

Fire in a confined area such as a mine, aircraft or a hotel room, frequently incapacitates and kills more from the smoke, poison gases and choking particles emitted than from the heat generated.

Oxygen levels often remain as high as 15-16% until just before the flashover point when the fireball moves through the whole of the confined area. Emergency self-rescue devices or smokehoods can therefore utilise catalytic oxidation of the CO to deal with that particular toxic component.

Filter self-rescue systems generally consist of adsorptive sections to remove toxic components, such as HCN, other acid gases and hydrocarbons, together with a catalytic system for the oxidation of carbon monoxide.

Rebreather systems typically provide supplemental oxygen by chemical means or pressure bottles. The CO_2 and H_2O are removed by appropriate adsorbents in the recirculating gas.

The filter systems need to cope with potentially high ambient CO levels and current draft standards are based on challenge gases containing 1% CO. Rebreather systems also have to deal with CO arising from potential leakage into the mask from the face and neck seal and from exhalation, but these levels will be lower.

Process Applications

Air fed to air-separation plants and compressors producing pressurised air for breathing purposes requires incoming air to be free of CO (and usually CO_2). Carbon dioxide, water and other contaminants can usually be adequately removed by the appropriate regenerable adsorbents, but carbon monoxide is not normally adsorbed sufficiently well.

Oxidation of trace CO can be achieved with catalysts described in this paper at typical compressor exit temperatures of $50\text{--}100^\circ\text{C}$, thus eliminating the need for additional preheat. Their ability to work at high relative humidity also eliminates the need for water vapour removal from the feed gas.

CATALYST DESIGN AND MANUFACTURE

The composition of almost any catalyst is dictated by the requirement for activity, stability and regenerability. In the case of a commercial precious metal catalyst, the economics of the process is an important consideration as well. The method of preparation, the precious metal precursors, the metal oxide/substrate, all have an important effect on the performance of the catalyst.

In certain applications, such as escape hoods where there may be no assisted gas circulation by fans, pumps or pressurised gas, the pressure drop across the catalyst is of particular importance.

Catalysts have therefore been produced in the form of impregnated cloth as well as granules of various configurations and the performance characteristics are discussed further on.

1. Precious metals/ SnO_2 in extrudate form.
2. Precious metals/ SnO_2 on highly adsorptive cloth fabric.
3. Precious metals/reducible metal oxide as an alternative non-tin oxide, low temperature CO oxidation catalysts, both on cloth fabric and in pellet form.

CATALYST TESTING AND EVALUATION

Three basic catalyst-activity testing methods have been adopted, depending upon the catalyst format and its final application. In all these tests, it is assumed that the only function of the catalyst being considered is the oxidation of CO in the presence of H_2O and CO_2 . Tests of complete devices always include the full range of poisons.

Filter Self-Rescuers or Smokehoods

Several draft test protocols are in existence for this type of device, including those issued by the United Kingdom Civil Aviation Authority, the Japanese and British Coal industry and others. There are differences, but in respect to CO removal, a typical challenge conditions would be:

1% CO
3.5% CO_2
balance air at > 80% R.H.
inlet temperature, 20°C or 37°C
gas flow - 30 l/min sinusoidal
 - 90 l/min constant

Performance requirements also vary but again typically would be:

exit CO, below 100 ppm
test duration, 20 minutes
total exit CO volume, < 200 cm^3
pressure drop, < $8.1\text{ cm H}_2\text{O}$

Both sinusoidal flow and constant flow, once-through testing has been applied to these low temperature CO oxidation catalysts. The testing conditions are given in the Appendix.

Recirculating Units (Both Static and Portable)

CO oxidation can of course be achieved by means of forced recirculation over the catalyst in a multipass mode. This is typical of either a rebreathing escape device or static environmental system, such as a submarine or diving chamber.

Typically, granular catalyst or monolith is used in these applications and the test protocol made specific to the duty required. The test itself can be run as once-through conversion or in recirculation mode. One specific test protocol used by UOP in once-through mode is

Test gas	:	1% CO in air
Flow rate	:	2.5 lmin ⁻¹
Pressure	:	atmospheric
Temperature	:	20-25 °C
Gas humidity	:	50-60%
Test duration	:	60 mins

Catalyst efficiency = CO reacted over 60 mins
$$\frac{\text{Total CO passed}}{\text{Total CO passed}} \times 100$$

Volume of CO reacted per gram of catalyst in cm³ gram⁻¹ is given by

$$\frac{\text{Flow rate (cm}^3\text{min}^{-1}\text{)} \times \text{time (mins)} \times \text{gas conc(\%)} \times \text{efficiency(\%)}}{\text{Weight of catalyst (grams)}}$$

Under these test conditions, the specified catalyst must convert 58 cm³ of CO or more per gram to be acceptable.

CATALYST PERFORMANCE

Tin Oxide Based Granular Catalyst

Precious metals on tin oxide is one of a range of fully commercial low temperature CO oxidation catalysts. It is made in extrudate form, it has an average bulk density of 1.5 gcm⁻³ and it is regenerable. This catalyst exhibits long-term stability

during the reaction and is not only tolerant to water vapour, it actually performs better in the presence of wet gas, as is evident in figure 1, which is a typical set of results. It has long shelf life when kept in a closed container. It tends to deactivate when left in the open (figure 2), but total reactivation is achieved by hydrogen reduction and slow passivation, as illustrated in figure 1. This catalyst outperforms hopcalite in 2 major respects.

1. It oxidises CO at room temperature and below.
2. It is tolerant to high relative humidity.

Figure 3 illustrates the activity results of 3 commercial catalysts, namely precious metals/ SnO_2 , precious metal/ Al_2O_3 and hopcalite, using test gas 1.5% CO in air. These results confirm the superiority of SnO_2 -based catalyst.

Tin Oxide Based Catalyst Cloth

Catalyst cloths for filter-type smokehoods have been prepared based on tin oxide with precious metals. Cloth was supplied by a variety of manufacturers, including Siebe Gorman, with surface areas of $1000 \text{ m}^2\text{g}^{-1}$ to $1200 \text{ m}^2\text{g}^{-1}$ and have all been used successfully to make active catalysts. The activity results of the 3 types of cloth are illustrated in figure 4.

As a result of the temperature sensitivity of the CO oxidation reaction, the performance of the catalyst at low temperature is dependent on the metal loading and dispersion. For instance a 30% drop in the tin loading, whilst keeping the precious metals level constant resulted in a failure at 25°C as per the prescribed test, but the catalyst passed the test at 37°C , as illustrated in figure 5. This is probably due to the surface kinetics manifesting itself at higher temperatures to help some species readily desorb or undergo rearrangement at the tin oxide sites. The temperature trend is further confirmed in figure 6, which shows the effect of initial test-bed temperature on activity. Consequently, for catalyst that is required to operate at an initial temperature of 37°C , the precious metal loading has been reduced to an optimum level.

STEM And ESCA Analysis Of Carbon Cloth Catalysts

The cloth specimens were ground to a fine powder, and a prewet carbon-coated nylon grid was dipped into the powder, allowed to dry and placed into the STEM for analysis. The metal particles

existed as highly dispersed clusters of precious metals/Sn. The clusters generally range in size from 2-6 nm. Particle-to-particle analysis showed good heterogeneous distribution of the metals on the fibres. Low quantities of Al and Zn were found to be associated with the fibres. It does not appear that these impurities have any significant effect on activity. ESCA results suggest that the calcination, reduction steps of this catalyst were effective at generating low oxidation states of the precious metals. The precious metals readily chemisorb oxygen on exposure to air, but the latter does not totally oxidise the precious metals from (0) to (II) oxidation state and is readily reactive with CO to form CO₂.

Alternative Non Tin Oxide Low Temperature CO Oxidation Catalysts.

Precious metal on reducible metal oxide deposited on high surface area cloth fabric (Ref. 1) have exhibited low temperature activity towards CO oxidation. The metal loadings used are broadly similar to those of SnO₂ type. The results are shown in figure 7. The tendency for the cloth to ignite fairly readily during processing, in particular, at the calcination step limits the temperature range and atmosphere that can be used to obtain the base oxide by thermal decomposition of nitrate precursors. In the case of precious metals/transition metal oxide catalyst supported on 2-3 mm diameter SiO₂ spheres, preliminary results indicate good low temperature CO oxidation activity. Figure 8 shows the effect on catalyst activity at room temperature. In the absence of the transition metal oxide, the initial activity is steadily lost, whereas when the catalyst contained the transition metal oxide, its activity is maintained over an extended period. The unsupported reducible metal oxides containing precious metals show equally good activity towards CO oxidation, as depicted in figure 9. These novel catalysts have potential application in breathable gases purification, in CO₂ lasers and in CO oxidation generally.

APPENDIX

Once Flow-Through Test

In the self-rescue filter device, the minimum performance requirement as laid down by UK Civil Aviation Authority is that the device shall provide the wearer a minimum duration of respiratory protection of 20 minutes against the challenge atmosphere, which contains, among other toxic gases, 3.5% CO₂ and 1% CO at 85% relative humidity. The specified CO inhalation limit of 100 ppm or 200 cm³ integrated volume shall not be exceeded at anytime.

The laboratory test that has been devised to meet the above specification has the catalyst operating in 2 regimes: initially at a lower workload representing the in-flight sedentary phase in an on-board emergency (taking into account anxiety during this phase which will increase respiratory rate) for a period of 10 minutes, rising to a higher workload for a further 10 minutes corresponding to an evacuation exercise, whilst keeping the CO level down to below 100 ppm over the whole 20-minute period.

Test Conditions

Test gas	: 1% CO, 3.5% CO ₂ in air
Catalyst temperature	: 20°C or 37°C
Relative humidity	: 85%
Pressure drop	: < 8.1 cm H ₂ O
Test duration	: 20 mins
Space velocity	: 12600 h ⁻¹ for 10 mins and 37000 h ⁻¹ for a further 10 mins
Performance requirement	: exit CO < 100 ppm or integrated CO volume slipped < 200 cm ³ over 20-min period.

Sinusoidal Flow Test

This test makes use of a breathing machine, which is basically a lung simulator, to provide a sinusoidal flow. It produces a mean flow of 30lmin⁻¹ of filtered air saturated with water at body temperature (37°C). The peak rate of flow is approximately π times the mean flow rate and the breathing frequency is 20 inspirations per minute. The test gases are 0.25% CO in air or 1.5% CO in air by volume at 95% relative humidity. The inhalation resistance must be less than 14 mbar.

Test Conditions

Test gas	: 0.25% CO or 1.5% CO in air
Lung capacity	: 1.5 l

Average flow rate	: 30 lmin ⁻¹
Peak flow rate	: 94 lmin ⁻¹
No of inspiration per min	: 20
Relative humidity	: 95%
Catalyst temperature	: 25°C or 37°C
Inhalation resistance	: < 14 mbar
Test duration	: time for 400 cm ³ of CO to slip, define as test life of catalyst.
Performance requirement	: Integrated CO slipped < 400 cm ³

Once Flow-Through Test (For Recirculating Units)

This test has been devised to meet the requirement of deep sea working habitats breathing atmosphere (Heliox = 80% He and 20% O₂), where the catalyst is used for scrubbing CO by recycling via a purification unit either on the sea bed or through an umbilical cord to the diving support vessel. In welding environment the CO level can rise in excess of 60 ppm. The TLV value for CO at atmospheric pressure is 50 ppm. In hyperbaric conditions (200 m depth, equivalent to 20 bar pressure), this figure is 2.5 ppm. Consequently, in a welding chamber habitat, the divers can be exposed to environmentally unacceptable level of CO, hence the need for CO scrubbing.

Test Conditions

Test gas	: 1% CO in air
Flow rate	: 2.5 lmin ⁻¹
Catalyst temperature	: 25°C
Relative Humidity	: 60%
Test duration	: 60 mins

Performance requirement : to convert 58 cm³ CO per minute per gram of catalyst.

REFERENCES

1. British Patent Application 89/6984.1

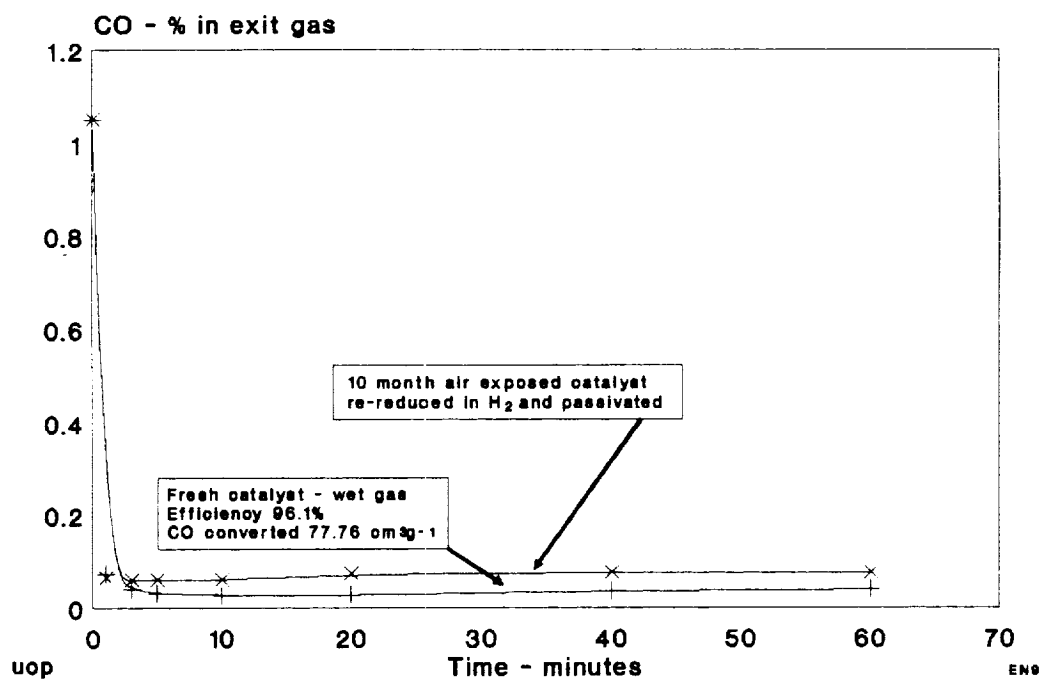


Fig.1 - Activity results of CO oxidation on precious metals/ SnO_2 / promoter using 1% CO in air (wet) at room temperature

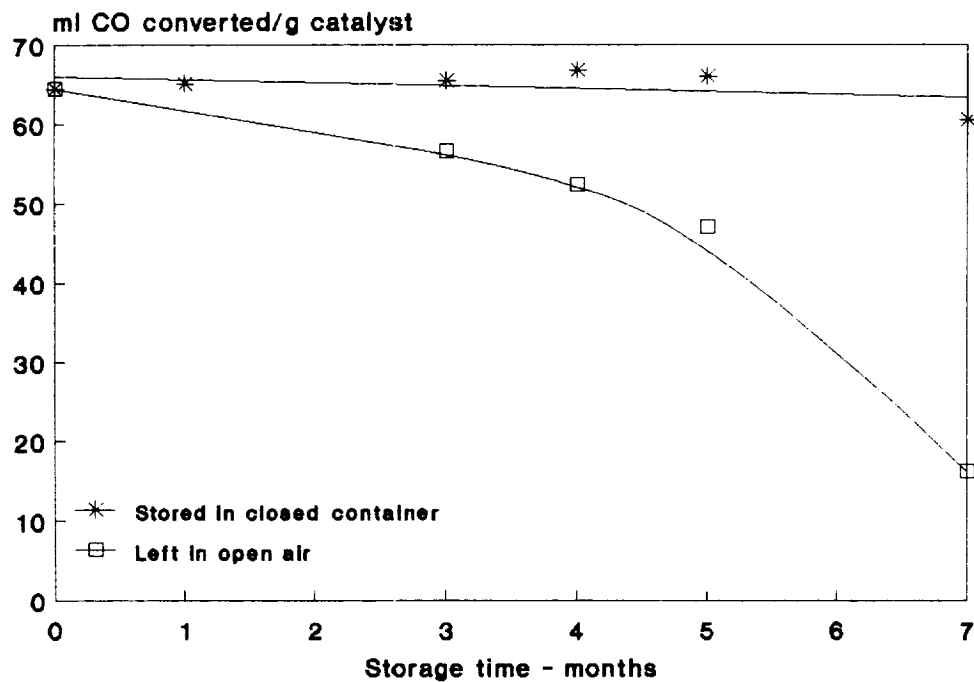


Fig.2 - Precious metals/ SnO_2 catalyst
Storage time vs. Activity test

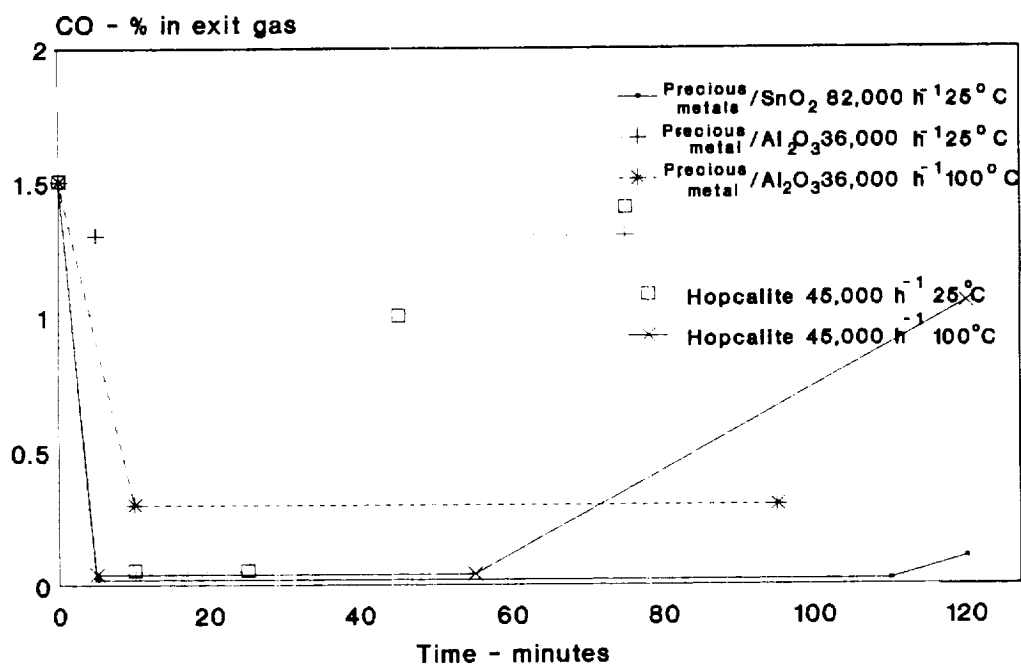


Fig.3 - Activity results of different CO oxidation catalysts - 1.5% CO in air

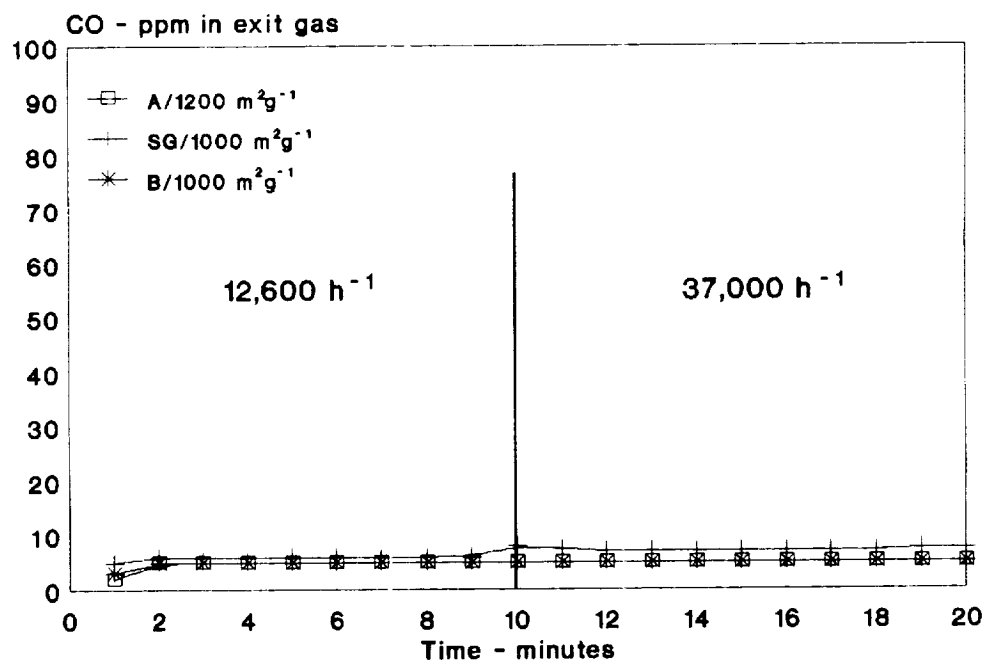


Fig.4 - Activity of various catalyst cloths at 25 °C
Test gas 1% CO, 3.5% CO_2 in air, (wet)

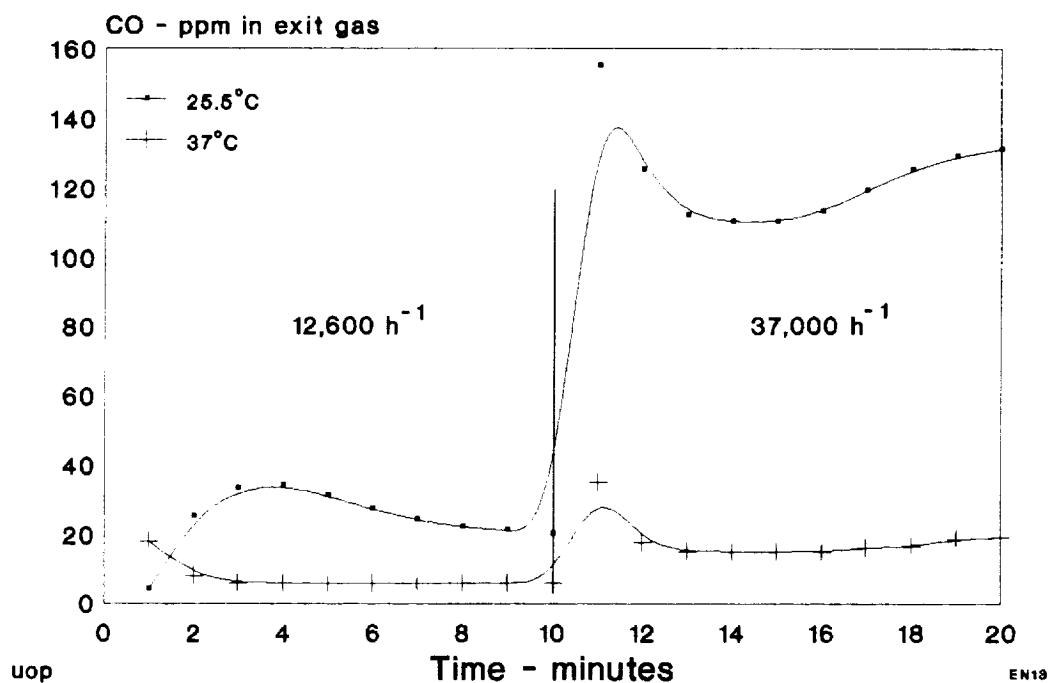


Fig.5 - Activity of cloth with 30% less Sn at 25.5°C & 37°C
Test gas 1% CO, 3.5% CO₂ in air (wet)

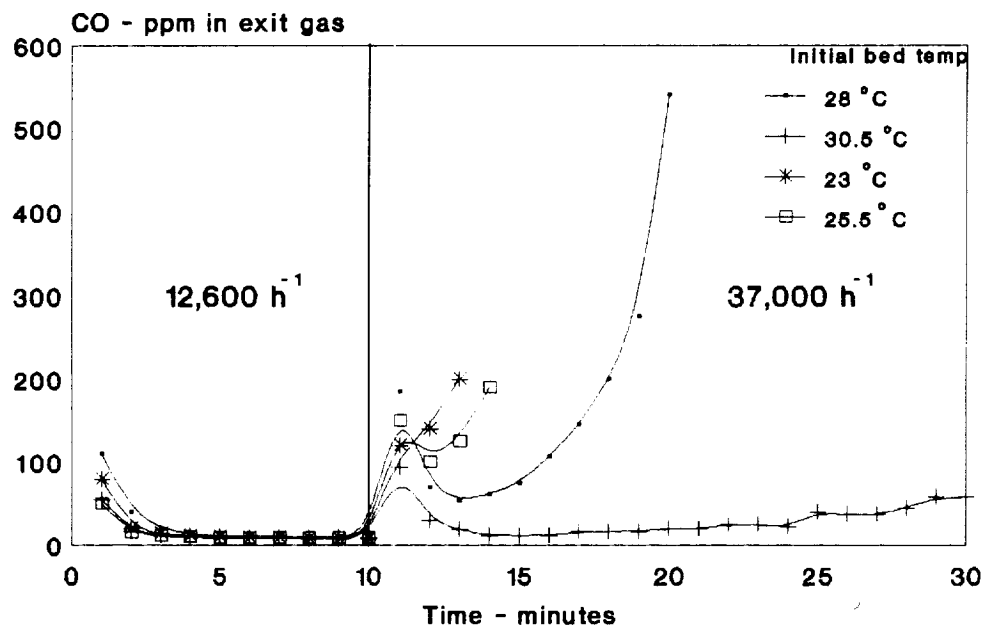


Fig.6 - CO oxidation of catalyst cloth A/1200 m²g⁻¹
at various temperatures.
Test gas 1% CO, 3.5% CO₂ in air, (wet)

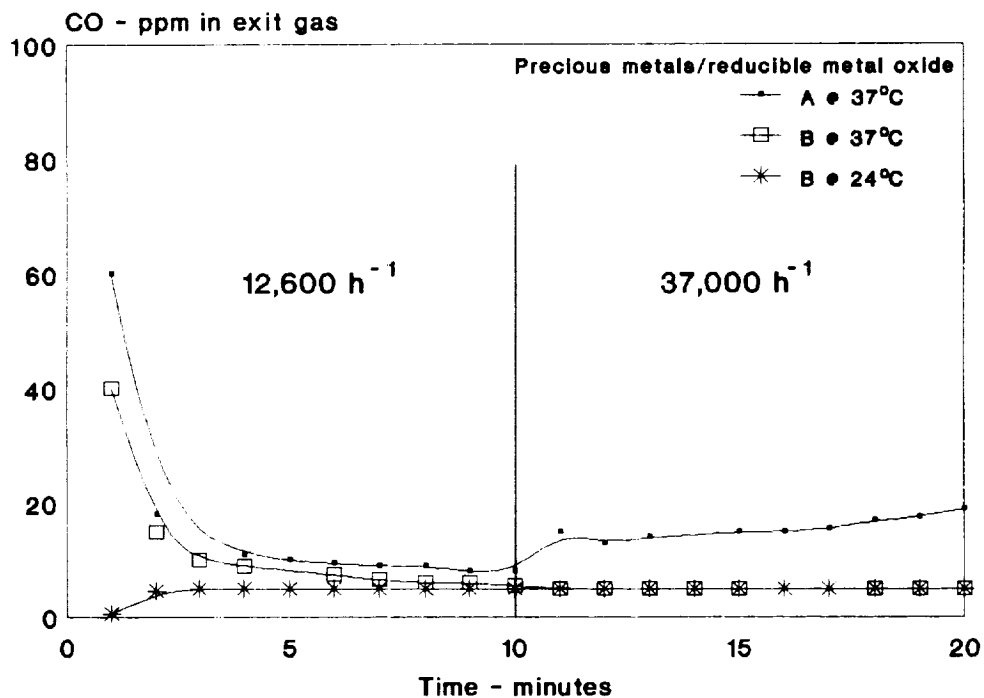


Fig.7 - Alternative low temperature CO oxidation on cloth fabric
Test gas 1% CO, 3.5% CO₂ in air, (wet)

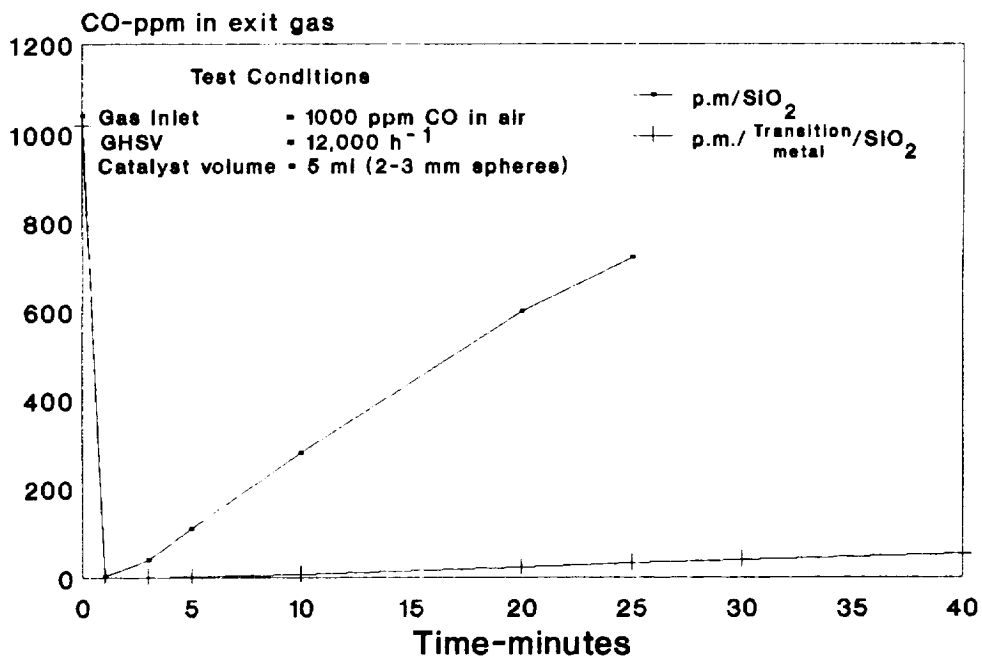


Fig.8 - Activity results of precious metals on SiO₂ and on Transition metal/SiO₂ at room temperature

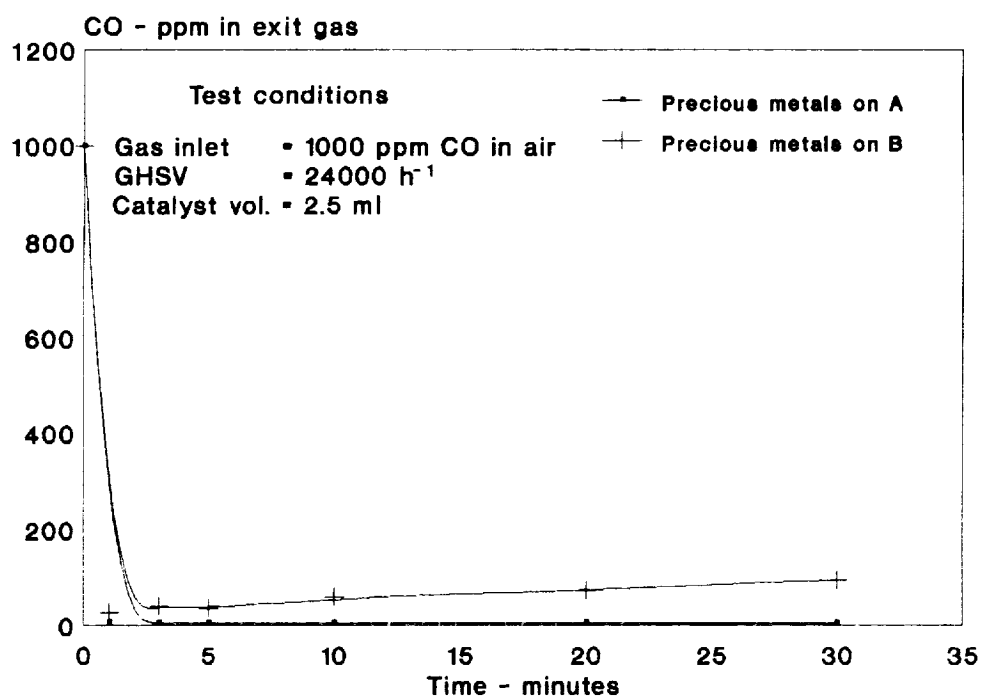


Fig.9 - Activity results of precious metals on reducible metal oxides A and B at room temperature